



TITLE:

# <International Research Center for Elements Science> Organotransition Metal Chemistry

AUTHOR(S):

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CITATION:

<International Research Center for Elements Science> Organotransition  
Metal Chemistry. ICR Annual Report 2005, 11: 56-57

ISSUE DATE:

2005-03

URL:

<http://hdl.handle.net/2433/65429>

RIGHT:

# International Research Center for Elements Science - Organotransition Metal Chemistry -

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## Scope of Research

This laboratory aims at establishment of new synthetic methodologies and new functional materials by designing well-defined catalysts based on transition metal chemistry. New concepts and ideas of molecular-based catalysts are accumulated by mechanistic investigations using kinetic techniques on the reaction intermediates and elementary processes. The research subjects include: (1) development of novel ligand systems for catalysis, (2) functionalization of organic substrates on transition-metal clusters, and (3) development of highly efficient ways of constructing functional organic molecules.

## Research Activities (Year 2004)

### Presentations

Highly Selective Ring-Opening Cross-Metathesis Reactions Using Fischer-type Carbene Ruthenium Catalysts, Katayama H, Fukuse Y, Nagao M, Ozawa F, The 3rd International Symposium of the Kyoto COE Project "Elements Science", 9 - 10 January, Kyoto, Japan.

Catalytic C-O Bond Cleavage of Allylic Alcohols Using Diphosphinidenecyclobutene-Coordinated Palladium Complexes, Ozawa F, Murakami H, Ishiyama T, Yoshifuji M (Tohoku Univ.), The 14th International Symposium on Homogeneous Catalysis, 5 - 9 July, Munich, Germany.

Facile and Selective Deallylation of Allyl Ethers Using Diphosphinidenecyclobutene-Coordinated Palladium Catalysts, Ozawa F, Murakami H, The 12th Japan-Korea Joint Symposium on Organometallic and Coordination Chemistry, 3 - 6 August, Sendai, Japan.

Bromination of Four Acetylenic Protons on  $\text{Cp}^*_4\text{Fe}(\text{HCCH})_2$ . Reactivity of the Resulting Bromoacetylene Fragments toward Nucleophiles, Okazaki M, Takano M (Tohoku Univ.), Ohtani T, (Tohoku Univ.) Tobita H

(Tohoku Univ.), Ogino H (The Univ. of the Air), The 12th Japan-Korea Joint Symposium on Organometallic and Coordination Chemistry, 3 - 6 August, Sendai, Japan.

Fischer-type Ruthenium Carbene Complexes: Highly Selective Catalysts for Ring-Opening/Cross Metathesis, Nagao M, The 2nd Trilateral Workshop on Organic Chemistry, 4 - 6 September, Kyoto, Japan.

Reaction Chemistry of Platinum-Group 14 Element Bonds, Ozawa F, JSCC Symposium 2004, 23 - 25 September, Kumamoto, Japan.

Stereocontrolled Synthesis and Photochemistry of *cis*-Poly(arylene vinylene)s, Katayama H, Nagao M, Nishimura T, Matsui Y, Akamatsu K (Konan Univ.), Nawafune H (Konan Univ.), Ozawa F, 50th Symposium of Organometallic Chemistry, Japan, 22 - 23 October, Tokyo, Japan.

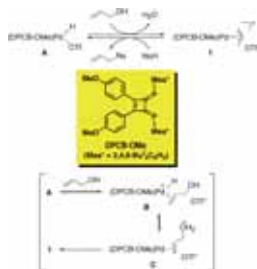
### Grants

Ozawa F, Reaction Control of Catalytic Intermediates, Grant-in-Aid for Scientific Research on Priority Areas, October 2002 - March 2006.

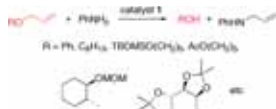
## Catalytic C-O Bond Cleavage of Allylic Alcohols and Ethers Using Diphosphinidenecyclobutene-Coordinated Palladium Complexes

We recently found that ( $\pi$ -allyl)palladium complex **1** bearing 1,2-bis(4-methoxyphenyl)-3,4-bis(2,4,6-tri-*tert*-butylphenyl)phosphinidene)cyclobutene (DPCB-OMe) efficiently catalyzes direct conversion of allylic alcohols into *N*- and *C*-allylation products under mild conditions. In this study, we have elucidated a novel catalytic mechanism given in Scheme 1 [1]. Thus, unlike common allylation reactions involving oxidative addition of a C-O bond to a Pd(0) species, the C-O bond of allylic alcohols is cleaved by the action of hydridopalladium complex **A**. Proton-transfer from the Pd to the OH group in **B**, followed by elimination of water from **C**, forms  $\pi$ -allyl complex **1**. We reasoned that strong  $\pi$ -accepting ability of DPCB-OMe ligand as an  $sp^2$ -hybridized phosphorus compound efficiently stabilizes **C** as a Pd(0) species by  $\pi$ -back-donation to facilitate the proton-transfer in **B**.

This novel catalysis is applied to deallylation of a variety of allyl ethers in aniline to give corresponding alcohols in high yields under mild conditions (Scheme 2) [2]. The reactions can be performed in air without loss of a variety of functionalities including vinyl, alkynyl, hydroxy, acetoxy, silyloxy, and acetal groups.



**Scheme 1.** Direct conversion of allylic alcohol catalyzed by (DPCB-OMe)Pd( $\pi$ -allyl) complex **1**.



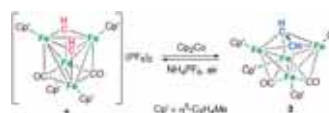
**Scheme 2.** Deallylation of allyl ethers catalyzed by **1**.

1. Ozawa, F.; Ishiyama, T.; Yamamoto, S.; Kawagishi, S.; Murakami, H.; Yoshifuji, M. *Organometallics* **2004**, 23, 1698.
2. Murakami, H.; Minami, T.; Ozawa, F. *J. Org. Chem.* **2004**, 69, 4482.

Ozawa F, Novel Organometallic Complexes with Phophaalkene Ligands: Synthesis and Catalysis, Grant-in-Aid for Scientific Research (B) (2), April 2003 - March 2006.

## Reversible Cleavage and Recombination of Acetylenic Carbon-Carbon Bond on a Tetra-iron Cluster Coupled with Two-Electron Redox Reaction

Two-electron reduction of **2** resulted in the coupling of two methylidyne ligands to afford **3** (Scheme 3) [3]. The point we wish to stress is that formation and cleavage of the carbon-carbon bond can be controlled on the Fe<sub>4</sub> core by two-electron reduction and oxidation. Two-electron oxidation of **3** led to the cleavage of the carbon-carbon bond to reproduce **2**. To our knowledge, our present study is the first example, in which the reversible carbon-carbon bond cleavage and formation occurs between acetylene and two methylidyne fragments via two-electron oxidation and reduction.

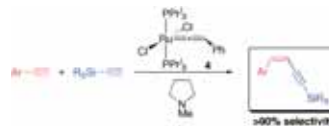


**Scheme 3.** Reversible carbon-carbon bond formation induced by two-electron redox reaction.

3. Okazaki, M.; Ohtani, T.; Ogino, H. *J. Am. Chem. Soc.* **2004**, 126, 4104.

## (*Z*)-Selective Cross-Dimerization of Aryl-acetylenes with Silylacetylenes Catalyzed by Vinylideneruthenium Complexes

Vinylideneruthenium complex **4** serves as good catalyst precursors for (*Z*)-selective cross-dimerization between arylacetylenes and silylacetylenes in the presence of *N*-methylpyrrolidine (Scheme 4). The reactions proceed at room temperature to afford (*Z*)-1-aryl-4-silyl-1-buten-3-yne in over 90% regio- and stereo-selectivities. The resulting enynes are efficiently desilylated by treatment with K<sub>2</sub>CO<sub>3</sub> in MeOH to give terminal alkenylacetylenes (ArCH=CH-C $\equiv$ CH) with (*Z*)-configurations.



**Scheme 4.** Ruthenium-catalyzed cross-dimerization between arylacetylenes and silylacetylenes.

## Award

Ozawa F, The BCSJ Award, Insertion of Phenylacetylene into [Pt(GeMe<sub>3</sub>)(SnMe<sub>3</sub>)(PMe<sub>2</sub>Ph)<sub>2</sub>], The Chemical Society of Japan, 15 July 2004.